

# Strong electron correlation effects in non-volatile electronic memory devices

M. J. Rozenberg,<sup>1,2</sup> I. H. Inoue,<sup>3</sup> and M. J. Sánchez<sup>4</sup>

<sup>1</sup>CPHT, Ecole Polytechnique, 91128 Palaiseau Cedex, France.

<sup>2</sup>Departamento de Física Juan José Giambiagi, FCEN, Universidad de Buenos Aires, Ciudad Universitaria Pabellón I, (1428) Buenos Aires, Argentina.

<sup>3</sup>Correlated Electron Research Center (CERC), National Institute of Advanced Industrial Science and Technology (AIST), Tsukuba 305-8562, Japan

<sup>4</sup>Centro Atómico Bariloche, (8400) San Carlos de Bariloche, Argentina.  
(Dated: February 2, 2008)

We investigate hysteresis effects in a model for non-volatile memory devices. Two mechanisms are found to produce hysteresis effects qualitatively similar to those often experimentally observed in heterostructures of transition metal oxides. One of them is a novel switching effect based on a metal-insulator transition due to strong electron correlations at the dielectric/metal interface. The observed resistance switching phenomenon could be the experimental realisation of a novel type of strongly correlated electron device.

PACS numbers: 85.30.Tv, 85.30.De, 73.40.-c

The inclusion of strong correlation effects in semiconductor electronic devices has long been a goal of solid state physicists. Significant progress has been achieved in recent years in studies of metal-insulator-metal (MIM) structures that display different types of resistance switching by the application of a voltage or current pulse; a prototype of two-terminal nonvolatile random access memories. The insulator of the MIM structure is either a transition metal oxide[1, 2, 3, 4, 5] or an organic material[6, 7], in which the electron correlations usually play an important role. The switching is directly related to the large hysteresis observed in the  $I$ - $V$  characteristics. These systems are collectively called resistance random access memories (RRAM) and the most fundamental current issues for this technology are the different hysteretic behaviour observed in the current-voltage characteristics and their relation to non-volatility.

The goal of the present work is to investigate the qualitatively different hystereses of  $I$ - $V$  curves in the MIM structures that have been experimentally observed so far, and to associate each hysteresis type to an appropriate physical mechanism. Our starting point is a recently introduced model for the RRAM device[8]. We shall first study the basic model predictions for the  $I$ - $V$  characteristics, and then show how it can be extended, incorporating the physics of strongly correlated effects.

The model assumes the existence of an insulating (and inert) medium with a nonpercolative structure of metallic domains that might correspond to defects, grains, phase separated regions, and so on[8]. Smaller domains are closer to the electrodes and are called “top” and “bottom”. A large domain occupies the bulk of the system that is called “central”. Carriers tunnel between domains under the action of an external electric field (or applied voltage). The probability of charge transfer depends on phenomenological parameters such as the tunneling rates, the number of states in the domains and

their occupation (see Ref. [8] for details). The model is mathematically defined by the following system of rate equations,

$$\frac{dn_i^b}{dt} = \Gamma_i^{eb} N_e n^e (1 - n_i^b) f_{eb}(V) - \Gamma_i^{bc} n_i^b N_c (1 - n^c) f_{bc}(V) \quad (1)$$

$$\frac{dn^c}{dt} = \sum_i [\Gamma_i^{bc} N_b n_i^b (1 - n^c) f_{bc}(V) - \Gamma_i^{ct} n^c N_t (1 - n_i^t) f_{ct}(V)] \quad (2)$$

$$\frac{dn_i^t}{dt} = \Gamma_i^{ct} N_c n^c (1 - n_i^t) f_{ct}(V) - \Gamma_i^{te} n_i^t N_e (1 - n^e) f_{te}(V) \quad (3)$$

where  $\Gamma_i^{\alpha\beta}$  denote the tunneling rates between the electrodes and domains, and  $\alpha, \beta = e, t, c, b$  denote “electrode”, “top”, “central” and “bottom”.  $N_\alpha$  is the total number of states in electrode or domain  $\alpha$ , and  $n^\alpha$  is the occupation.  $f_{\alpha\beta}(V)$  describes the dependence of the transfer probabilities between  $\alpha$  and  $\beta$  on the given external voltage protocol  $V(t)$ . The subindex  $i$  labels the domains.

To gain a qualitative understanding of the model, we make some simplifying assumptions. We ignore disorder effects and take all “top” and “bottom” domains to be identical. The functions  $f_{\alpha\beta}(V)$  are assumed to be independent of  $\alpha$  and  $\beta$ . We also take a unique tunneling rate for the two interfaces  $\Gamma^{et} = \Gamma^{be} \equiv \Gamma^{ext}$  and similarly inside the dielectric  $\Gamma^{tc} = \Gamma^{cb} \equiv \Gamma^{int}$ . Therefore, we can just consider the behaviour of the “average” top and bottom domain occupations, that we denote  $n^t$  and  $n^b$ . Finally the metallic electrodes are assumed half-filled.

The set of equations simplifies to three coupled nonlinear differential equations,

$$\frac{dn^b}{dt} = [\Gamma^{ext} \frac{N_e}{2} (1 - n^b) - \Gamma^{int} n^b N_c (1 - n^c)] f(V) \quad (4)$$

$$\frac{dn^c}{dt} = [\Gamma^{int} N_b n^b (1 - n^c) - \Gamma^{int} n^c N_t (1 - n^t)] f(V) \quad (5)$$

$$\frac{dn^t}{dt} = [\Gamma^{int} N_c n^c (1 - n^t) - \Gamma^{ext} n^t \frac{N_e}{2}] f(V) \quad (6)$$

that have to be solved for the unknown  $n^\alpha(t)$  with  $\alpha = t, c, b$ . The coefficients  $f(V)$  are time dependent through the applied voltage protocol  $V(t)$ . There is no general solution for this model, but specific cases can be analysed. As the central domain is taken to be large compared to top and bottom, we may assume that its occupation remains approximately constant, *i.e.*,  $\frac{dn^c}{dt} \approx 0$  and  $n^c(t) \approx n_o^c$ . Under this condition, the system of Eqs. (4)–(6) can be formally solved and the result for the time dependent bottom domain occupation is,

$$n^b(t) = e^{-\int_0^t P(t') dt'} \left( \int_0^t Q(t') e^{\int_0^{t'} P(t'') dt''} dt' + n^b(0) \right) \quad (7)$$

where  $P(t) = f(V)[\Gamma^{int} N_c(1 - n_o^c) + \Gamma^{ext} N_e/2]$  and  $Q(t) = f(V)[\Gamma^{ext} N_e/2]$ . The occupation of top is simply given by,  $n^t(t) = 1 - [(1 - n_o^c)/n_o^c]n^b(t)$ . Taking the time derivative on both sides we see that  $n_o^c$  controls the charge accumulation in the model, that is,  $[dn^t/dt - dn^b/dt]$ .

Equation (7) provides further insight into the non-volatility properties. As the system is strictly always out of equilibrium under applied voltage, the key quantity to consider is the relaxation time under either applied bias  $V_b$  or during a voltage pulse  $V_p$  ( $V_b \ll V_p$ ). The main dependence of the relaxation time comes from the first exponential factor of (7). With the rather natural assumption that the tunneling probability dependence is  $f(V) \sim e^V$ , one finds that the ratio of relaxation times is exponential in  $(V_p - V_b)$ . Thus bias relaxation can be made orders of magnitude slower than the switching time, which is consistent with the observed behavior in actual systems. We further note that when the device is disconnected from the external battery there remains an internal voltage  $V_{int}$  due to the inhomogeneous charge distribution. The coulombic forces would produce the subsequent relaxation of this state, and this process is crucial for the long time non-volatility characteristics of a system[8]. The previous analysis implies the existence of a compromise: driving the system to a strong charge inhomogeneous state (with a strong or long  $V_p$  pulse) would provide a desired large set/reset resistance ratio but, on the other hand, would also lead to faster relaxation, *i.e.*, shorter non-volatility time. These results are quite consistent with the investigations of relaxation in Nb-doped SrTiO<sub>3</sub>/LaTiO<sub>3.5</sub>/Au heterostructures[9].

Let us now turn to the predictions of the model for the  $I$ - $V$  characteristics and hysteresis effects. The applied voltage protocol is  $0 \rightarrow V_{max} \rightarrow -V_{max} \rightarrow 0$  with a constant sweep velocity. For simplicity, all three domains are assumed to be initially half filled. Following Simmons and Verderber[10], we take the function  $f(V) = \sinh(kV)$  where  $k$  depends on various material parameters, thus we set  $k = 1$ . The (positive) current in and out of the system is given by the carriers entering the bottom domain and leaving the top domain respectively. In Fig.1 we show the results for two qualitatively different hystereses that

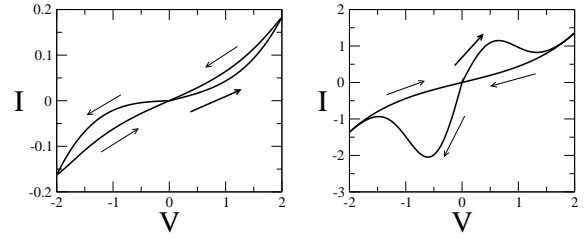


FIG. 1: Current-voltage characteristics.  $N_t = N_b = 10^6$ ,  $N_c = 10^{10}$  and  $\Gamma^{int} = 2 \times 10^{-8}$ ,  $\Gamma^{ext} = 6 \times 10^{-14}$  (left panel) or  $\Gamma^{int} = 8 \times 10^{-9}$ ,  $\Gamma^{ext} = 6 \times 10^{-12}$  (right panel). The  $V$  protocol cycle begins at the thick arrow.

the model predicts depending on the choice of parameters. Their main difference is that one shows low to high current switching (left) while the other shows the opposite behavior (right). It is not difficult to understand the reason for this contrast. The current out (for current in, a similar analysis can be done) depends mainly on the filling level of the top domains. The larger their occupation, the more carriers that are available to tunnel out. During the positive side of the voltage protocol,  $V$  is initially increased and then decreased down to zero. During this phase, charge is transferred from the center domain to the top and from there to the electrode. Therefore, if more charge enters the top domain than leaves it, the filling level during the increasing positive- $V$  ramp would be lower than the filling level during the subsequent decreasing positive- $V$  ramp. This would lead to low-to-high current switching as shown in the left panel. Therefore, the qualitative form of the hysteresis depends on the intrasystem (top/center and bottom/center) charge transfers compared to the interface (top/electrode and bottom/electrode) ones, both of which are controlled by the model parameters (basically the  $\Gamma N$  products). Assuming larger *interface* transfers should be appropriate for systems such as Au/SiO/Au studied in the pioneering work of Simmons *et al.*[10, 11], where hysteresis and negative differential resistance (NDR) were observed and qualitative agreement with our model is found, as shown in the right panel of Fig.1. On the other hand, larger *intrasystem* transfer is a likely assumption for the heterostructures with transition metal oxide dielectric, where electronic inhomogeneous states are often realized. It would also be the case for the system of artificially created domains of Al-nanoclusters, where, in fact, hysteresis similar to the results shown in the left panel of Fig. 1 has been observed[7].

While the present model provides useful insight for the analysis of relaxation times and basic switching mechanisms[8], the qualitative predictions for hysteresis effect illustrated above show a notable limitation; namely, the  $I$ - $V$  curves *never cross* at the origin. Experimentally, *crossing*  $I$ - $V$  characteristics are often observed[1, 2, 3, 5, 6], thus providing an important mo-

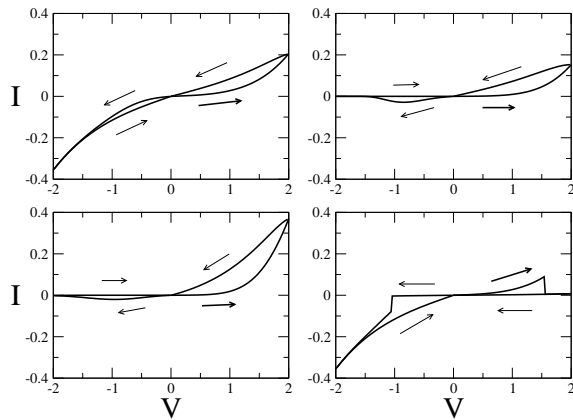


FIG. 2: Current-voltage characteristics.  $N_t = N_b = 10^6$ ,  $N_c = 10^{10}$ ,  $\Gamma^{int} = 6 \times 10^{-8}$ ,  $\Gamma^{ext} = 10^{-13}$  and  $n^t(0) = n^b(0) = n^c(0) = 0.1$ . Basic model (top left), model with interface charge dependent tunneling (top right), idem with Schottky effect (bottom left), model with occupation driven Mott transition and  $\Delta/T = 3$  (bottom right). The  $V$  protocol cycle begins at the thick arrow.

tivation to consider two extensions of the basic model, Eqs. (1)–(3), that we shall describe next.

The first one is to incorporate the physics of interface tunneling rates that depend on the charge accumulation, *i.e.*, the dependence of  $\Gamma^{ext}$  with  $n^t$  and  $n^b$ . The underlying physical mechanism is similar to the dependence of the depletion width with impurity concentration in ohmic contacts of metal/semiconductor interfaces[12]. Basically, the accumulated charge density at the interface produces additional band bending that leads to a reduction in tunneling, thus enhancing  $\Gamma^{ext}$ . Borrowing from standard junction tunneling theory[12] we can qualitatively model this dependence as  $\Gamma_{t,b}^{ext} = e^{-1/\sqrt{n^{t,b}+1}} \Gamma^{ext}$  (Ref. [13]) so the tunneling is enhanced with increasing charge accumulation in the small interface domains right up to the saturation value  $\Gamma^{ext}$  for fully occupied domains, *i.e.*,  $n^{t,b}=1$ . This mechanism is widely assumed to be relevant for many resistance switching phenomena, however it is also usually linked to *poor non-volatility* characteristics.

We incorporated this effect in our basic set of Eqs. (4)–(6) and solved for the model behavior. The results are shown in Fig. 2 (top right) along with the predictions of the original basic model (top left) for the same parameter set (for reference). We see that, in fact, this additional assumption is sufficient to turn the hysteresis into the *crossing* type, a result that can be understood through a similar analysis to that we described earlier[8]. An important point to mention here is that the hysteresis effect does not necessarily need to take place at both electrodes simultaneously, since the large center domain acts as a buffer that effectively decouples the two interfaces. Hence this mechanism would also be relevant for systems with two different interfaces where the switching properties

are controlled by one of them, *e.g.* in heterostructures such as Au/PbTiO<sub>3</sub>/La<sub>0.5</sub>Sr<sub>0.5</sub>CoO<sub>3</sub> where the Au interface forms a Schottky barrier but La<sub>0.5</sub>Sr<sub>0.5</sub>CoO<sub>3</sub> does not[1]. To investigate a possible effect of Schottky barriers in our results, we modified the voltage dependent part of the tunneling function to the form  $f(V) = e^V - 1$  (forward bias) that produces Schottky type  $I$ - $V$  characteristics. The results are shown in Fig. 2 (bottom left) and we find no qualitative differences in the hysteresis.

As we mentioned before, this mechanism is often linked with poor non-volatile characteristics, possibly because it lacks a stabilisation effect that could lengthen the lifetimes of the charge-accumulated (or -depleted) metastable states. A physical mechanism that would enable such stabilisation is likely to be due to a *coherent* effect in which many particles act in a correlated manner. Here we propose that such a mechanism is based on a Mott metal-insulator transition taking place in the domains when they become close to half filling. In fact, this occupation (or doping) driven metal-insulator transition is a strong correlation effect found throughout the transition metal oxide series[14] and even in some organic materials[15]. For concreteness, we shall assume that the domains undergo a Mott transition when they are close to half-filling. On becoming insulating, the domains open an insulating gap  $\Delta$  in their excitation spectrum which we model by assuming a reduction in the density of states at the Fermi energy given by  $D = e^{-\Delta/T} D_0$ ,  $T$  being the temperature. The dependence of the density of states at the Fermi energy was entered implicitly in our equations through a multiplicative factor (set to unity) in the function  $f(V)$ , since we were always concerned with tunneling between metallic domains. We now consider this effect explicitly by modifying  $f(V)$  in the model Eqs. (4)–(6) to  $f_{mit}(V) = e^{-\Delta/T} f(V)$  if the occupation of the corresponding domain is within 10% of half-filling, or else  $f_{mit}(V) = f(V)$ . The results are shown in Fig. 2 (bottom right). The results can be understood as follows. Initially, the domains are assumed to be lightly filled, *i.e.* in the metallic state. As the applied voltage is increased, charge is accumulated at the top domains thus increasing their occupation level. Eventually, when they approach half-filling, they become insulating and open a Mott gap. The tunneling probability to and from the top domain gets dramatically reduced, with a consequent drop in the output current and also in the rate of further charge injection. With the reduced charge injection, the occupation level of the domain remains about constant and the current is low for the rest of the positive voltage sweep ( $\rightarrow V_{max} \rightarrow 0$ ). This is also the case for the beginning of the negative voltage sweep, as the *leakage* of charge out of the top domain is also greatly suppressed (*thus providing an enhanced non-volatility of the high resistance state*). Eventually a large negative  $V$  drives enough charge out of the top domains and once again they become metallic, their correlation gap closes and the system switches back

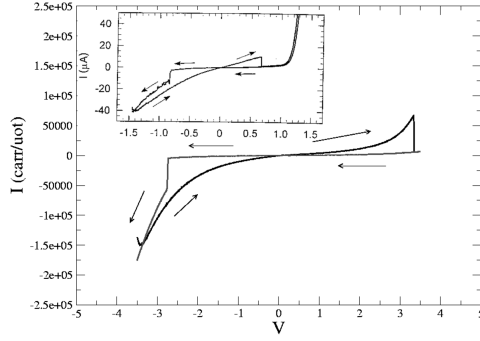


FIG. 3: Current-voltage characteristics for the model with occupation driven Mott transition. The model parameters are  $N_t=N_b=10^6$ ,  $N_c=10^9$  and  $\Gamma^{int}=10^{-13}$ ,  $\Gamma^{ext}=3\times 10^{-14}$ . The current is in carriers per unit of time (ie, Monte Carlo step). Inset: experimental  $I$ - $V$  characteristics in Au/SrTiO<sub>3</sub>/SrRuO<sub>3</sub> from Ref. [16].

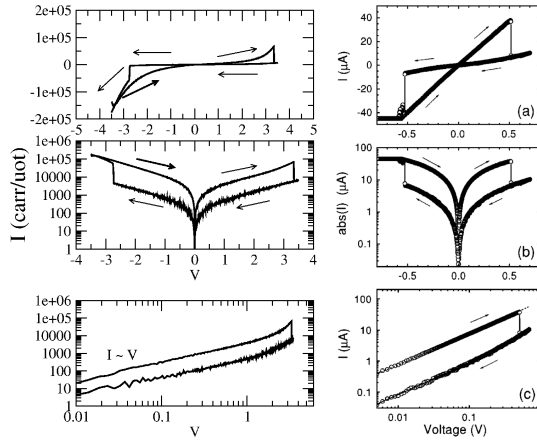


FIG. 4: Idem as in Fig. 3 in normal scale (top), semi-log scale (middle) and log-log scale (bottom). The left panels show experiments in Au/SrZrO<sub>3</sub>/SrRuO<sub>3</sub> from Ref. [2].

to a high current state.

In order to give further support to this mechanism we performed Monte Carlo simulations[8] on the model given by Eqs. (1)–(3) supplemented with the Mott transition effect. We looked for parameters that qualitatively reproduce the experimental results in the MIM structures with Cr-doped SrTiO<sub>3</sub> or SrZrO<sub>3</sub> of the IBM group[2, 16]. Our results are shown in Fig. 3 and the experiments are shown in the inset. (We modified the voltage protocol to  $-V_{max} \rightarrow V_{max} \rightarrow -V_{max}$  to match the experiment.) Not only is the qualitative agreement very satisfactory, several details are also worth pointing out. The initial occupation level of the domains that allow best comparison to the experimental data was found to be small (around

10%), consistent with the fact that the systems are nominally empty band insulators with only light doping due to the Cr substitution. Moreover, the intriguing sudden high to low current switching at positive applied bias in the experiment is a feature that naturally emerges from our domain-doping driven metal to insulator transition scenario. In Fig. 4 we make more detailed comparison to the experimental data by plotting the  $I$ - $V$  characteristics in different scale types, all of which show excellent qualitative agreement with experiment. We note that while the current is proportional to  $V$  at low voltages the system is never truly ohmic in the sense that there is no actual sample current, rather a series of very incoherent charge transfer processes. In fact, current conduction in these systems is known to be non-filamentary[2].

To conclude, we have proposed a model for resistance memory switching and find the different physical mechanisms that lead to various qualitatively different hysteresis effects in the  $I$ - $V$  characteristics. We proposed a new scenario for memory switching in strongly correlated transition metal oxide heterostructures, based on a metal-insulator transition driven by charge injection (doping) to domain structures in physical proximity to interfaces. The information (high resistance state) is stored by driving the systems to a qualitatively different state which, at the same time, provides a novel mechanism for the enhancement of the non-volatility. Our model results are supported by excellent qualitative agreement with experimental data in various heterostructures.

We would like to thank Y. Tokura, M. Kawasaki, A. Sawa and A. Odagawa for valuable comments and discussions. We also acknowledge N. E. Hussey for critical reading of this paper. Support from Fundaci3n Antorchas, UBACyT and ANCTyP is acknowledged.

- 
- [1] P. W. M. Blom *et al.*, Phys. Rev. Lett. **73**, 2107 (1994).
  - [2] A. Beck *et al.*, App. Phys. Lett. **77**, 139 (2000).
  - [3] Y. Watanabe *et al.*, App. Phys. Lett. **78**, 3738 (2001).
  - [4] S. Q. Liu, N. J. Wu, and A. Ignatiev, Appl. Phys. Lett. **76** 2749 (2000).
  - [5] N. A. Tulina, A. M. Ionov and A. N. Chaika, Physica C **366**, 23 (2001).
  - [6] D. M. Taylor and C. A. Millis, J. Appl. Phys. **90**, 306 (2001)
  - [7] L. Ma *et al.*, App. Phys. Lett. **82**, 1419 (2003).
  - [8] M. J. Rozenberg, I. H. Inoue and M. J. Sánchez, Phys. Rev. Lett. **92**, 178302 (2004).
  - [9] A. Schmehl, *et al.*, App. Phys. Lett. **82**, 3077 (2003).
  - [10] J. G. Simmons and R. R. Verderber, Proc. Roy. Soc. A **301**, 77 (1967).
  - [11] A. B. Pakhomov *et al.*, J. Phys.: Condens. Matter **14**, 5355 (2002).
  - [12] S. M. Sze, *Physics of Semiconductor Devices*, (Wiley, New York, 1981).
  - [13] H. C. Casey, *Devices for Integrated Circuits*, (Wiley, New York, 1999).

- [14] M. Imada, A. Fujimori and Y. Tokura, Rev. Mod. Phys. **70**, 1039 (1998).
- [15] H. Mori *et al.*, J. Am. Chem. Soc. **124**, 1251 (2002).
- [16] A. Beck *et al.*, International Patent (PCT), WO00/49659 (2000).